STUDIES IN PURIFICATION OF BIOGAS USING ALGAE IN SEWAGE WASTE WATER-
A REVIEW PAPER

PROF. S. V. KHEDKAR, PAYAL N. BHAUTIK
Department of Chemical Engineering, College of Engineering and Technology, Akola

Accepted Date: 13/03/2015; Published Date: 01/04/2015

Abstract: Biogas is an alternative energy source produced from the anaerobic digestion of organic matter by bacteria. It is composed primarily of methane and CO2 with trace amount of other gases such as H2S. The presence of CO2 decreases energy yield in biogas; however it imparts a quenching effect making it non explosive. Past studies have used expensive and environmentally harmful chemicals to purify biogas. This study involves the concentration of biogas purification system by utilizing microalgae to metabolize and remove CO2 from the system. We established a model of microalgae closed batch photo bioreactor with the goal of capturing CO2 present in the biogas. The biogas purification process was applied in order to increase the calorific value. For this system the growth profile of microalgae cultivated with concentrations of CH4 and CO2 were analysed as well as physical chemical and biological process. Biogas which constitutes 40% CO2 and 60% of CH4. This result demonstrates a high tolerance of microalgae cultures to upgrade biogas by increasing the efficiency of methane in the biogas. The calorific value of the biogas after purification with microalgae cultivation and thus approaching to more calorific value of pure methane.

Keywords: Biogas, Methane, Carbon Dioxides, Micro-Algae, Sewage etc

Corresponding Author: PROF. S. V. KHEDKAR

Co Author: MR. S. R. SUREKA

Access Online On:
www.ijpret.com

How to Cite This Article:
S. V. Khedkar, IJPRET, 2015; Volume 3 (8): 95-108
INTRODUCTION

Microalgae production facilities can thus be fed biogas from activated tannery sludge can significantly increase the quality of methane by scrub out the CO2. Conceptually the algae cultivation near the biogas plant is fairly simple. The idea is to pipe the biogas from anaerobic reactor to the closed suspended batch algae cultivation system. The inlet and outlet gas is analysed by the gas analyser Orsat apparatus. The microalgae species selected for this study exhibited growth under high CO2 concentration.

Biogas is produced in many different environments, including in landfills, sewage sludge and during anaerobic degradation of organic material. Biogas is comprised of methane (CH4, about 45-75% by volume), carbon dioxide (CO2, 25-55%), and other compounds including hydrogen sulfide (H2S, present in concentrations from several hundred to a couple of thousand parts per million), water, and other trace gas compounds. Methane is a powerful greenhouse gas if emitted into the atmosphere, but can also represent a valuable renewable energy source, with the potential to reduce GHG emissions when it is collected and substituted for fossil fuels.

Raw biogas produced from digestion is roughly 60% methane and 39% CO2 with trace elements of H2S; it is not high quality enough to be used as fuel gas for machinery. The corrosive nature of H2S alone is enough to destroy the internals of a plant.

The solution is the use of biogas upgrading or purification processes whereby contaminants in the raw biogas stream are absorbed or scrubbed, leaving more methane per unit volume of gas. There are four main methods of upgrading: water washing, pressure swing adsorption, selexol adsorption, and amine gas treating.

<table>
<thead>
<tr>
<th>Component</th>
<th>Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>45–70%</td>
<td>60%</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>25–55%</td>
<td>35%</td>
</tr>
<tr>
<td>Water vapour</td>
<td>0–10%</td>
<td>3,1%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0,01–5%</td>
<td>1%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0,01–2%</td>
<td>0,3%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0–1%</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0,01–2,5 mg/m³</td>
<td>0,7 mg/m³</td>
</tr>
<tr>
<td>Hydrogen Sulphide</td>
<td>0–30’000 mg/m³</td>
<td>500 mg/m³</td>
</tr>
</tbody>
</table>
Water washing / Scrubbing

The most prevalent method is water washing whereby high pressure gas flows into a column in which the carbon dioxide and other trace elements are scrubbed by cascading water running counter-flow to the gas. This arrangement can deliver 98% methane with manufacturers guaranteeing maximum 2% methane loss in the system. It takes roughly between 3% and 6% of the total energy output in gas to run a biogas upgrading system.

Water scrubbing is used to remove CO2 and H2S from biogas since these gases are more soluble in water than methane. The absorption process is purely physical. Usually the biogas is pressurized and fed to the bottom of a packed column while water is fed on the top and so the absorption process is operated counter-currently. Water scrubbing can also be used for selective removal of H2S since H2S is more soluble than carbon dioxide in water. The water which exits the column with absorbed CO2 and/or H2S can be regenerated and re-circulated back to the absorption column. Regeneration is accomplished by de-pressuring or by stripping with air in a similar column. Stripping with air is not recommended when high levels of H2S are handled since the water quickly becomes contaminated with elementary sulfur which causes operational problems. When cheap water can be used, for example, outlet water from a sewage treatment plant, the most cost efficient method is not to re-circulate the water.

Chemical Absorption

Chemical absorption involves formation of reversible chemical bonds between the solute and the solvent. Regeneration of the solvent, therefore, involves breaking of these bonds and correspondingly, a relatively high energy input. Chemical solvents generally employ either aqueous solutions of amines (i.e. mono-, di- or tri-ethanolamine) or aqueous solution of alkaline salts (i.e. sodium, potassium and calcium hydroxides).
Figure 2: Flow chart of chemical absorption process

Biswas et al. (1977) reported that bubbling biogas through a 10% aqueous solution of monoethanolamine (Nelder and Mead) reduced the CO2 content of biogas 40 to 0.5–1.0% by volume. MEA solution can be completely regenerated by boiling for 5 min and is then ready for re-use. The advantages of chemical absorption are complete H2S removal, high efficiency and reaction rates compared to water scrubbing, and the ability to operate at low pressure. Because of these advantages, the process is commonly used in industrial applications, including natural gas purification (Kim et al., 2004; Palmeri et al., 2008). The disadvantages are the additional chemical inputs needed and the need to treat waste chemicals from the process. The final price of upgraded biogas using this technique is estimated to be €0.17 per Nm3 biogas, according to De Hullu et al. (2008).

Pressure Swing Adsorption

Figure 3: Pressure-swing adsorption schematic

PSA using zeolites or activated carbon at different pressure levels is an effective method for the separation of CO2 from methane (Grande and Rodrigues, 2007; Pinto et al., 2008). Activated carbon impregnated with potassium iodide can catalytically react with oxygen and H2S to form water and sulfur (Pipatmanomai et al., 2009). The reaction is best achieved at 7 to 8 bar (unit of pressure) and 50 to 70oC. The activated carbon beds also need regeneration or replacement.
when saturated. The advantages of PSA technology are more than 97% CH4 enrichment, low power demand, and low emission and removal of nitrogen and oxygen. The main disadvantage of PSA technology is an additional H2S removal step needed before PSA. Also, tail gas from PSA still needs to be treated. The process is also relatively more expensive than some others; according to De Hullu et al. (2008), the cost of PSA method is 0.40 €/Nm3 biogas.

**Membrane**

H2S Removal Compressor Biogas Membrane separator internally. Solid membranes can be constructed as hollow fiber modules or other structures which give a large membrane surface per volume and thus very compact units. Typical operating pressures are in the range of 25-40 bars. The underlying principle of membrane separation creates a trade-off between high methane purity in the upgraded gas and high methane yield. The purity of the upgraded gas can be improved by increasing the size or number of the membrane modules, but more of the methane will permeate through the membranes and be lost.

![Membrane biogas purification process](image)

**Figure 4: Membrane biogas purification process**

There are two membrane separation techniques: high pressure gas separation and gas-liquid adsorption. The high pressure separation process selectively separates H2S and CO2 from CH4. Usually, this separation is performed in three stages and produces 96% pure CH4. Gas liquid adsorption is a newly developed process that uses micro-porous hydrophobic membranes as an interface between gas and liquids. The CO2 and H2S dissolve into the liquid while the methane (which remains a gas) is collected for use (Chatterjee et al., 1997; Harasimowicz et al., 2007). The advantages of membrane separation are that the process is compact, light in weight, has low energy and maintenance requirements and easy processing. The disadvantages of membrane separation are relatively low CH4 yield and high membrane cost. According to De Hullu et al. (2008), the cost of membrane method is 0.12 €/Nm3 biogas. Although this cost is low in comparison to other methods reviewed, difficulties with yield and purity as well as the
potential for fouling membranes (requiring membrane replacement) raises operating costs and strongly impacts project economics.

**Bio-filter**

Biological processes are widely employed for H2S removal, especially in biogas applications. Because chemical use is limited, they are often economical and environmentally friendly (Duan et al., 2006; van der Zee et al., 2007). The use of chemotropic bacterial species (*Thiobacillus* genus) to condition biogas is well established. Microalgae cultures have also been examined but the available literature is short and cannot help in appropriately evaluating this option. Another methodology deploys anaerobic phototrophic bacteria (*Chlorobium limicola*) capable of oxidizing H2S in the presence of light and CO2. No known commercial applications at this time use phototrophic bacteria. The following text therefore focuses on chemotrophic bacteria.

On the other hand, some thiobacteria (i.e., *Thiobacillus novellus, Thiothrix nivea*) can grow either heterotrophically or autotrophically, having the capability of using available organic material as carbon source (i.e., glucose, amino acids). Biogas, which contains around 30% CO2, is a good source of inorganic carbon, rendering it more suitable for autotrophic bacteria. Under limited oxygen conditions, *Thiobacillus* bacteria evoke a redox-reaction which produces S0 (Equation 1). Conversely, an excess oxygen condition will lead to SO42− generation and, thus, acidification, as shown in equation

\[
\text{H2S} \leftrightarrow \text{H}^+ + \text{HS}^- \quad \text{(dissociation)}
\]

\[
\text{HS}^- + 0.5\text{O}_2 \rightarrow \text{S}0 + \text{OH}^- \quad (1)
\]

\[
\text{HS}^- + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+
\]

Chung et al. (1996) isolated *Thiobacillus thioparus* from swine wastewater. The bacteria were immobilized with Caalginate to produce pellet-packing materials for a lab-scale biofilter (5-cm diameter, 25-cm working length). Growth was optimum at pH 6–8 under facultative autotrophic and heterotrophic conditions. The biofilter was operated under air-H2S mixture flow between 36 to 150 L/h containing 5 to 100 ppmv of H2S. Removal efficiency was more than 98% at residence times higher than 28 s. Optimal S-loading was 25 g m−3 h−1. The main product was (i) S0 (72%) at high H2S concentration (60 ppmv), and (ii) sulfate (75%) at low H2S concentration (5 ppmv). No pH fluctuation was observed. The experiments showed no temperature influence on removal efficiency between 20° and 37°C.
Thiobacillus ferroxidans, another potential bacterial species, is an example of a chemotrophic aerobe which can oxidize FeSO4 to Fe2(SO4)3. The resultant Fe3+ solutions are capable of dissolving H2S and oxidizing it to S0. This allows S0 separation and permits biological FeSO4 regeneration. These bacteria are acidophilic and are able to grow at low pH levels (1 to 6). The main biochemical reaction is detailed in Equation 2.

$$2\text{FeSO}_4 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \quad (\text{pH} = 2) \quad (2)$$

Acidithiobacillus thiooxidans AZ11 has been isolated and incubated from H2S-enriched soil (Lee et al., 2006). The bacteria can live in a very acidic environment, as low as pH = 0.2, with high sulfate concentration (74 g/l). A lab-scale biofilter (4.6 cm diameter, 30 cm working length) was inoculated with these inocula on a crushed, porous ceramic support. The study showed that, at a low flow rate (space velocity = 200 h/1) and residence time of 18 s, this species was capable of degrading high H2S concentration (2200 ppmv) and S-loading of 670 g/(m3*h). Removal efficiency ranged from 94% to 99.9% and was demonstrated to be dependent on residence time (the studied range was 6 to 18 s).

Figure 5 shows a biological H2S scrubber designed by Soroushian et al. (2006), consisting of a fiberglass tank packed with plastic media and a makeup water recirculation pump. With this system, H2S levels were maintained at below the 40-ppmv target level by the scrubber under normal operating conditions, but low temperature and nutrient deficiency could lower microbial activity levels and resulted in a pH drop. The H2S containing gas enters the absorption section and is washed by scrubbing liquid. The liquid has an alkaline nature (pH 8–8.5) and absorbs the H2S. The biogas exits the top of the absorber virtually free of H2S. The sulfide containing liquid flows into the bioreactor. In the reactor bacteria oxidize the sulfide with oxygen. The sulfur is then removed by use of a settler. The sulfide-free liquid returns to the absorption section.

![Biological H2S removal system](image-url)
The advantages of biological methods are low energy requirement, mild conditions and the elemental sulfur byproduct. Sulfur can be re-used for the production of sulfuric acid, hydrogen sulfide or agricultural applications (Kim et al., 2002; Vannini et al., 2008). Biological methods also have some disadvantages: additional nutrients are required for growing bacteria, and a small amount of O2 and N2 are left in treated biogas. The H2S removal efficiency depends on the activity of bacteria. Bench-marking studies show that the method described above is cost effective up to 40 tons per day.

**Cryogenic Separation**

Cryogenic separation of biogas is based on the fact that CO2, H2S and all other biogas contaminants can be separated from CH4 based on the fact that each contaminant liquefies at a different temperature-pressure domain. This separation process operates at low temperatures, near -100oC, and at high pressures, almost 40 bars. These operating requirements are maintained by using a linear series of compressors and heat changers.

![Schematic of cryogenic separation](image_url)

**Figure 6: Schematic of cryogenic separation**

Crude biogas streams through the first heat exchanger which cools the gas down to 70°C. This heat exchanger makes use of the product stream as cooling medium, which is energy efficient and has the advantage of preheating the upgraded biogas before leaving the plant. The first cooling step is followed by a cascade of compressors and heat exchangers which cool the inlet gas down to -100oC and compress it to 40 bars before it enters the distillation column. Finally, the distillation column separates CH4 from the other contaminants, mainly H2S and CO2.

The main advantage of cryogenic separation is the high purity of the upgraded biogas (99% CH4), as well as the large quantities that can be efficiently processed. The main disadvantage of cryogenic separation is that cryogenic processes require the use of considerable process equipment, mainly compressors, turbines and heat exchangers. The need for the equipment...
raises capital and operating costs relative to other options. The final price of upgraded biogas using this technique is estimated to be €0.44 per Nm3 biogas (De Hullu et al., 2008).

Purification of Biogas using METHODOLOGY

- **MICROALGAE** Mixture of microalgae collected from the waste water treatment plant and it was maintained in the laboratory by culturing it in a sterilized 200mL Erlenmeyer flask with 100 mL of Chu 10 medium (Chu 1942). The culture was incubated at 32°C under constant illumination of160 μmol/m2-s with aeration of the culture by the addition of biogas at 5%, 10% and 25% respectively. After several microalgae cultivation the most tolerant microalgae of the genus *Nannochloropsis* and this material was used in the experiment proposed. This proposed wild species mainly by its lower sensitivity to climatic conditions, contaminants and low sensitivity to temperature changes.

- **MICRO ALGAL CULTURE MEDIUM AND CHEMICALS** This study used the digestion of tannery sludge, collected from leather industry; normal tap water with trace amount of nutrient was added to the culture at ratio of 10%. The tannery sludge was stored in plastic drum 500mL capacity and transported to the laboratory. Inoculate 1mL of sample to 100mL of algae culture medium in 200-250 mL Erlenmeyer conical flask. All the flaks were placed on a lab line force bench top orbital open air shaker at 100 rpm under the fluorescent lamp.

**PHOTO BIOREACTOR** The diagram of experimental apparatus used in this study is described in figure 1. The photo bioreactor was built with a Pyrex glass tank of 7cm diameter height 20cm and the nominal volume of 1,500mL. The air or gas from the digester is supplied through an inlet at the bottom of the reactor, passing through the dispersion system in the centre of the column. Thus the air flow runs throughout the column.

![Figure 1- Experimental equipment closed batch suspended photo bioreactor model.](image-url)
Sampling port arranged at the left to collect the sample at various depth. Dome at the top to collect gas. Gas outlet tube ended with a flow meter.

The aeration of the blowing air and biogas was controlled with flow meter, a flow rate of 80 mL/min during the period of maximum radiation of fluorescent lamp at a concentration 160 μmol/m²-s of 100mL of gas which leads to a concentration of 40% CO₂ with 60% CH₄ in biogas injected into the cultivation. Variations in cell density of microalgae cultivation throughout the development was monitored daily by counting cells under a microscope (X10) with the aid of a Neubauer chamber (Improved Chamber). The cell density was expressed as number of cells per millilitre of culture (Cell.ml⁻¹) an average of the three counts with the experimental cell density was prepared according to the time charts (day) (Soares, 2009). The biomass of the culture was measured during the experiment to calculate the maximum productivity using equation.

\[
\text{Equation 1: PRODUCTIVITY (P) } \frac{g.l - 1. day - 1}{Time \text{ final} - Time \text{ initial}} = \frac{\text{Dry weight final} - \text{Dry weight initial}}{Time \text{ final} - Time \text{ initial}}
\]

Environmental Impact

The environmental impact of the upgrading processes is an important factor that can be used to compare the different techniques. If the pollutants that are removed from biogas during upgrading are emitted in the atmosphere, the contamination of the environment will run counter to the goal of producing an environmentally-friendly fuel to replace current fossil fuels. Environmental impacts for each process were therefore considered, with concerns summarized briefly below.

Chemical Absorption

The only process streams other than biogas needed in the absorption process is a liquid water phase containing a catalyst. This either can be amines for the absorption of CO₂ or Fe/EDTA complexes for the absorption of H₂S. During the upgrading process CO₂ is emitted in the atmosphere as a waste stream. The used amine solution must be replaced a few times a year and thus is also a waste. This solution can be separated into a water phase and the amines using a membrane. The clean water phase can then be purged to a river.

High Pressure Water Scrubbing

The water scrubbing process contains two main waste streams. The first waste stream is the exhaust of air which was used to strip the regenerated water. This stream mainly consists of air enriched in CO₂ but also contains traces of H₂S and CH₄. Because H₂S is rather poisonous, this
stream needs to be treated. And because CH4 is far more damaging to the environment than CO2 the CH4 in this stream should be burned. The second waste stream consists of water which is purged and replaced with clean water to keep dissolubility as high as possible and avoid accumulations of CO2 and H2S. Because most of the CO2 and H2S will be absorbed in the stripper during the gas phase the purge stream does not have to be treated.

Pressure Swing Adsorption

Besides the product stream (upgraded biogas, containing more than 97% CH4), the pressure swing adsorption process creates a waste stream, which contains all the adsorbed material from the molecular sieves. Among other things, some significant amounts of CH4 are found in this waste stream. Normally, the CH4 is burned to avoid emissions. Often, the waste stream leads to a gas engine linked to a generator. Alternatively, the waste stream can be recycled back through the adsorption process, which reduces the amount of CH4 in the waste stream and increases the yield of CH4 in the product stream.

The fact that cryogenic separation uses no chemicals makes this separation an environmental friendly technique, though the process uses considerable energy. The only waste stream consists of a high percentage of CO2 with traces of H2S and CH4. As in other processes, because H2S is rather poisonous and CH4 is more damaging to the environment than CO2, this stream needs to be treated.

Membrane Separation

The waste gas still contains CH4 which is highly polluting. Part of it can be fed back into the inlet or, as in pressure swing absorption, the waste gas can be burnt in a gas engine linked to a generator. Using a multistage setup also increases the yield. Positive results have been found using an internally staged permeator. Electrical use is low since only a compressor has to be powered. The generator can power the compressor which results in an even higher CH4 efficiency. The CO2 stream is then of no further use.

CONCLUSION

The purification method gives 97% to 99% of pure methane gas. The purification methods studies have used expensive and environmentally harmful chemicals to purify biogas compare to biogas purification using microalgae. In biogas purification using algae there is sewage waste water is used as media for cultivation of algae which consumed CO2 from the raw biogas and purified up to 98% very economically and environment friendly.
REFERENCES


